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Coupling Reactions of *ortho*-Substituted Aryl Halides with Alkynes. The Synthesis of Functionalized 1-Naphthyl-, 1-(1-Naphthyl)-2-phenyl-, and 1,2-Bis(1-naphthyl)acetylenes

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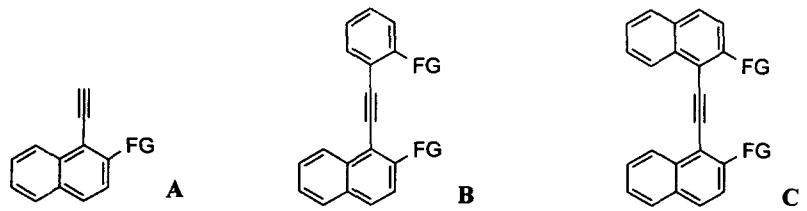
Abstract: Coupling of 2-functionalized 1-naphthyl halides with gaseous acetylene, (trialkylsilyl)acetylenes, and aryl acetylenes under $Pd(PPh_3)_4$ or $Pd(PPh_3)_4$/CuI catalysis has been investigated to prepare 1-naphthyl-, 1-(1-naphthyl)-2-phenyl-, and 1,2-bis(1-naphthyl)acetylenes with various *ortho* substituents, *i.e.*, the $-CH_3$, $-CH_2OH$, $-CO_2Me$, and $-CH_2OCH_2C{\equiv}CCH_3$ groups. The reaction conditions have been optimized (yields up to 96 %) by changing halogen atom in aryl halides, solvent, alkyl in (trialkylsilyl)acetylenes, and catalyst (Pd(0) *vs.* Pd(0)/Cu(I)). In case of 1-naphthyl iodide with a tethered alkyne unit, coupling has been observed to compete with a cascade of intramolecular Heck-type reactions. The mechanism of β-elimination of a hydridopalladium species has been discussed. 1-Naphthyl bromide bearing the $-CO_2Me$ group has been found to be susceptible to nucleophilic aromatic substitution with a solvent. The successful synthesis of an unsymmetrical 1-(1-naphthyl)-2-phenylacetylene derivative has been shown to depend critically on combination of aryl halide/aryl acetylene.

INTRODUCTION

Aryl-alkyne bond-forming reactions mediated by transition metals have been routinely used in modern acetylene chemistry.[1,2] Two general synthetic methods have been exploited most frequently: The coupling reaction of aryl halides/triflates with terminal alkynes under Pd[3,4] or Pd/Cu[4,5] catalysis and, alternatively, with metallated (Sn[6], Zn[7]) alkynes under Pd catalysis.[4]

In spite of a continuous development of the aryl-alkyne coupling methodology, the reactions of *ortho*-substituted 1-naphthyl halides with acetylenic compounds to give 2-functionalized 1-ethynylnaphthalene derivatives (**A**-**C**; FG = a functional group) have not been systematically studied. Only scattered examples of preparation and use of these compounds may be found in literature.[8]



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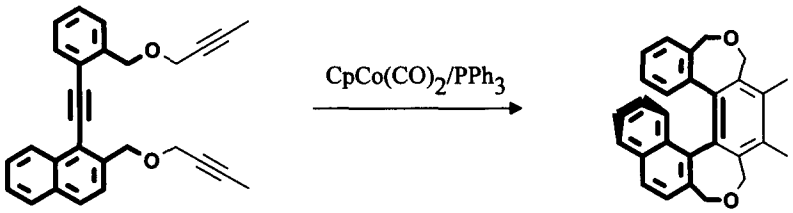
Recently, we have demonstrated the use of functionalized 1,2-diarylacetylenes in the synthesis of molecules with helical chirality[9] (Scheme 1).



1 2

Scheme 1

In order to explore the scope and limitations of this novel synthetic approach to screwed molecules, we had to prepare 1-ethynylnaphthalenes of the type **A-C** (Figure 1) representing building blocks for the synthesis of the key triynes, *e.g.*, **1** (Scheme 1). We report herein a systematic study on the coupling reaction of 2-substituted 1-naphthyl halides with gaseous acetylene as well as terminal alkynes under Pd(0) or Pd(0)/Cu(I) catalysis.

RESULTS AND DISCUSSION

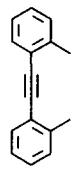
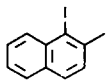
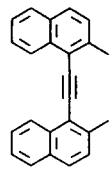
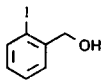
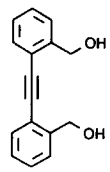
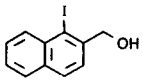
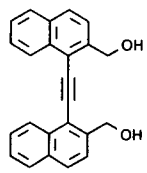
Coupling reactions of aryl halides with gaseous acetylene

Ortho-substituted 1-naphthyl halides have been found to differ from the corresponding phenyl derivatives by reaction with gaseous acetylene under Pd(0)/Cu(I) catalysis (Table 1). The most striking contrast in reaction ability was observed at hydroxymethylated aryl halides: The coupling of 2-iodobenzyl alcohol **5** with acetylene afforded the product **9** in excellent yield but the analogous transformation of the naphthyl counterpart **6** totally failed. $Pd(PPh_3)_4$-CuI and piperidine were the best catalyst system/solvent combination we found.[13]

Competition between the aryl-alkyne coupling and intramolecular Heck-type reaction

On treatment with terminal alkynes, the naphthyl iodide **11** exhibited a dichotomous behavior depending on a catalyst system and alkyne used. Under $Pd(PPh_3)_4$ catalysis, the compound **11** reacted with gaseous acetylene to provide the coupled product **12** in satisfactory yield. At the same time, the presence of an internal alkyne moiety susceptible to an intramolecular Heck-type reaction allowed generation of the side product **13** (Table 2, entry 1). In order to prevent its formation, CuI co-catalysis was applied (Table 2, entry 2).

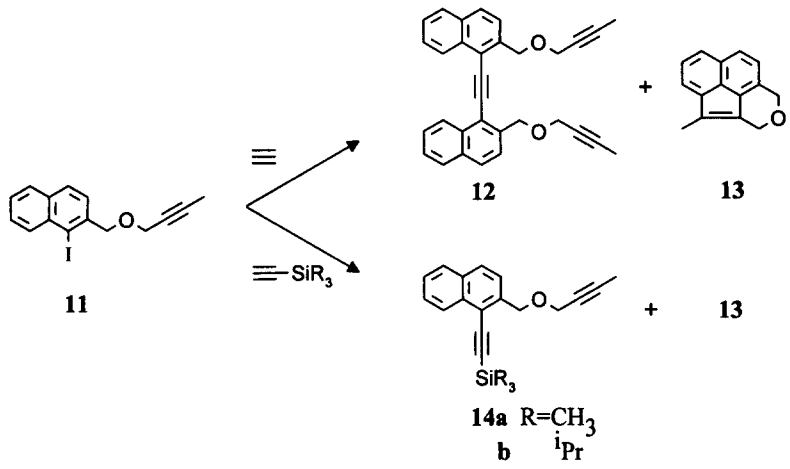
Table 1. Coupling Reactions of *ortho*-Substituted Phenyl *vs.* 1-Naphthyl Halides with Gaseous Acetylene

entry	educt		$Pd(PPh_3)_4$ (mol%)	CuI (mol%)	cond.[a] (°C, h)	product		yield[b] (%)
1		**3**	1.5	3	80°, 0.3		**7**[c]	96
2		**4**	5	10	80°, 1.5		**8**[c]	81
3		**5**	1	2	rt, 1		**9**[c]	94
4		**6**	5	10	80°, 20		**10**	0[d]

[a]In piperidine under 1 atm pressure of gaseous acetylene. [b]Isolated. [c]See refs 10-12. [d]A complex mixture of products was formed.

The outcome of coupling of iodide **11** with (trialkylsilyl)acetylenes depends on bulkiness of the trialkylsilyl moiety. On treatment with (trimethylsilyl)acetylene under $Pd(PPh_3)_4$ catalysis, the reaction gave rise to a mixture of **14a** and **13** (Table 2, entry 3) demonstrating again a competition between two possible reaction pathways: Aryl-alkyne coupling (to give **14a**) and a cascade of intramolecular Heck-type reactions (to give **13**). Attachment of the sterically demanding triisopropylsilyl group to acetylene suppressed the former pathway so that the Heck-type cyclization prevailed in the reaction (Table 2, entry 4). In accordance, in the absence of any terminal alkyne, the $Pd(PPh_3)_4$-catalyzed cyclization of iodide **11** afforded **13** as the sole product of the reaction (Table 2, entry 5).

Table 2. The Aryl-Alkyne Coupling Reaction *vs.* the Intramolecular Heck-Type Reaction

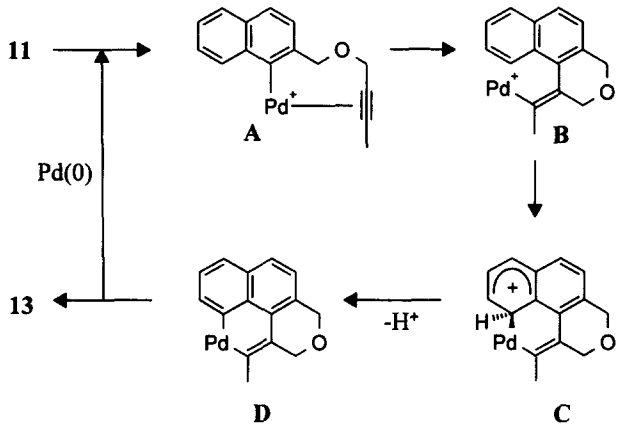


entry	acetylene (equiv)	cond.[a]	time (h)	product	yield[b] (%)
1	HC≡CH (excess)	A	1	**12** **13**	30 8
2	"	B	3	**12**	49
3	Me_3Si-C≡CH (2.3)	A	3	**14a** **13**	15[c] 11
4	$^iPr_3Si$-C≡CH (1.3)	A	20	**13**	38
5	0	A	40	**13**	41[d]

[a]A: $Pd(PPh_3)_4$ (5 mol%), piperidine, 80 °C; B: CuI (10 mol%), for further conditions see method A. [b]Isolated. [c]A complex mixture of polar products was formed. [d]A 23% recovery of the starting material.

The formation of compound **13** is explained in Scheme 2.[14] Assumedly, oxidative addition of a Pd(0) species across the Ar-I bond of **11** produces a σ-aryl palladium(II) complex **A** that is consumed in an intramolecular insertion reaction of the tethered alkyne unit affording a tricyclic σ-vinyl palladium(II) complex **B**. Subsequently, the adjacent π-electron system of naphthalene is intramolecularly attacked by

palladium as an electrophile to create a cationic palladium(II) intermediate[15] **C** and, after a proton loss, a palladacycle **D**. The reaction cascade is completed by reductive elimination to give rise to the tetracyclic product **13**.



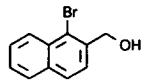
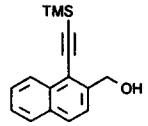
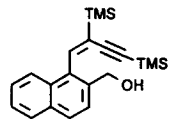
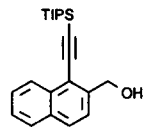
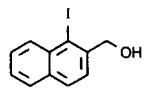
Scheme 2

Coupling reactions of aryl halides with (trialkylsilyl)acetylenes

The reaction course and preparative yields of coupling 1-naphthyl halides with (trialkylsilyl)acetylenes have been found to be affected by halogen atom, *ortho* substituent, bulkiness of the trialkylsilyl group in alkyne, and solvent (Tables 3 and 4). On treatment with (trimethylsilyl)acetylene under $Pd(PPh_3)_4$ catalysis, the bromo alcohol **15** afforded the ethynylated naphthalene **16a** in low yield along with the side product **17** (Table 3, entry 1) that arose from **16a** by a subsequent carbopalladation. Reduction of the amount of (trimethylsilyl)acetylene (*e.g.*, 1.0 equiv) did not prevent the formation of **17** and, moreover, the reaction did not reach completion. Replacement of the bromide **15** with the iodo alcohol **6** suppressed the carbopalladation but the yield of **16a** was not improved (Table 3, *cf* entries 1 and 3).

A marked improvement was achieved by using (triisopropylsilyl)acetylene instead of its trimethysilyl analogue. Although the bulkier alkyne reacted with 1-naphthyl halides more sluggishly, the coupling provided higher yield of aryl acetylene and carbopalladation did not take place. Starting from bromo alcohol **15**, the product **16b** was obtained in a moderate yield (Table 3, entry 2). Finally, the use of iodide **6** in reaction with (triisopropylsilyl)acetylene resulted in an excellent yield of the coupled product **16b** (Table 3, entry 4).

Table 3. Coupling Reactions of *ortho*-Substituted 1-Naphthyl Halides with Trialkylsilyl Acetylenes

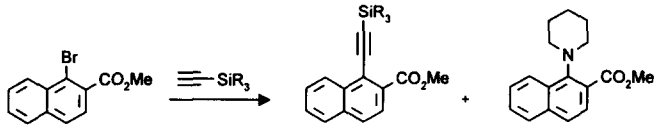
entry	educt		acetylene[a] (equiv)	$Pd(PPh_3)_4$ (mol%)	cond.[b] (°C, h)	product		yield[c] (%)
1		**15**	A, 2.2	5	80°, 12[d]		**16a**	25[e]
							**17**[f]	8[e]
2		**15**	B, 1.2	5	80°, 17		**16b**	60
3		**6**	A, 2.2	5	80°, 2.5		**16a**	25
4		**6**	B, 1.2	5	80°, 40		**16b**	96

[a]A: Me_3Si-C≡CH, B: $^iPr_3Si$-C≡CH. [b]In diisopropylamine unless noted otherwise. [c]Isolated. [d]In piperidine. [e]A 80% conversion of the starting material. [f]Position of substituents and configuration at the double bond were determined by NMR using COSY, ROESY, and HMBC experiments.

Competition between the aryl-alkyne coupling and nucleophilic aromatic substitution

The coupling reaction of bromo ester **18** with silylated acetylenes has been observed to compete with a displacement of the bromine atom by the solvent (Table 4). On treatment of bromide **18** with (trimethylsilyl)acetylene under $Pd(PPh_3)_4$ catalysis in piperidine, the coupled product **19a** arose along with the solvolysis product **20** (Table 4, entry 1). Under exclusion of the ethynylation reagent solvolysis afforded the nitrogen derivative **20** regardless of the presence or absence of $Pd(PPh_3)_4$ (Table 4, entry 2). These results disprove a palladium-catalyzed amination of the naphthyl bromide[16] and suggest a nucleophilic aromatic substitution proceeding *via* a classical Ad_N+E_β mechanism. The use of a sterically encumbered amine suppressed the undesirable solvolysis of **18**. 2,2,6,6-Tetramethylpiperidine allowed to obtain **19b** in good yield (Table 4, *cf* entries 1 and 3).

Table 4. Coupling Reactions of Methyl 1-Bromo-2-naphthoate with Trialkylsilyl Acetylenes[a]



18 **19a** R=Me **b** ^{i}Pr **20**

entry	acetylene[b] (equiv)	solvent	time (h)	product	yield[c] (%)
1	A, 2.2		10	**19a** **20**	27 19
2	0	"	24	**20**	41[d]
3	B, 1.2		14	**19b**	67

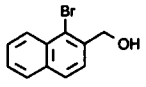
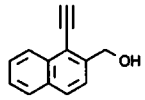
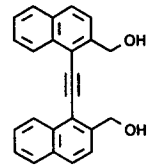
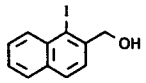
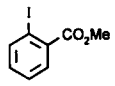
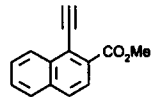
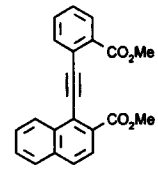
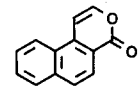
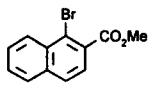
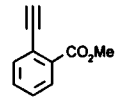
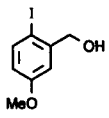
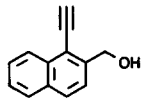
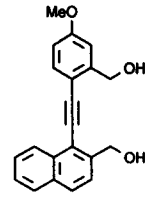
[a]$Pd(PPh_3)_4$ (5 mol%), 80 °C. [b]A: Me_3Si-C≡CH, B: $^{i}Pr_3Si$-C≡CH. [c]Isolated. [d]The same result was obtained in the absence of the palladium complex.

Coupling reactions of aryl halides with aryl acetylenes

The reactions of naphthyl acetylene **23** with naphthyl halides demonstrated a strong effect of halogen atom identity. Whereas bromide **15** did not give any diol **10** (a complex mixture of products was formed; Table 5, entry 1) iodide **6** afforded **10** in a good yield (Table 5, entry 2).

In addition, the synthesis of unsymmetrical bisaryl-acetylene derivative **26** revealed importance of an appropriate choice of reaction partners. On treatment of phenyl iodide **21** with naphthyl acetylene **24** under $Pd(PPh_3)_4$ catalysis, both the educts were consumed but only the isochromenone derivative **27** was isolated from the reaction mixture (Table 5, entry 3). In contrast, a combination of naphthyl bromide **18** with phenyl acetylene **25** gave the desired diester **26** in an excellent yield (Table 5, *cf* entries 3 and 4). Finally, unsymmetrical diol **28** was prepared by reaction of iodo alcohol **22** with naphthyl acetylene **23** under $Pd(PPh_3)_4$ catalysis in good yield (Table 5, entry 5).

Table 5. Coupling Reactions of *ortho*-Substituted Aryl Halides with *ortho*-Substituted Aryl Acetylenes

entry	educt[a]		acetylene		$Pd(PPh_3)_4$ (mol%)	CuI (mol%)	cond.[b] (°C, h)	product		yield[c] (%)
1		**15**		**23**	5	10	rt, 22		**10**	0[d]
2		**6**		**23**	5	10	40°, 20		**10**	77
3		**21**		**24**	10	0	80°, 3		**26**	0[e]
									**27**	31
4		**18**		**25**	5	0	80°,50[f]		**26**	93
5		**22**		**23**	10	10	80°, 1[f]		**28**	61

[a]Equimolar amounts of aryl halide and aryl acetylene. [b]In piperidine unless noted otherwise. [c]Isolated. [d]A complex mixture of products was formed. [e]A 43% recovery of the starting material. [f]In diisopropylamine.

CONCLUSION

Coupling of 2-functionalized 1-naphthyl halides with gaseous acetylene, (trialkylsilyl)acetylenes, and aryl acetylenes under Pd(0) or Pd(0)/Cu(I) catalysis has been shown to provide 1-naphthyl-, 1-(1-naphthyl)-2-phenyl-, and 1,2-bis(1-naphthyl)acetylenes. Tuning reaction conditions by changing halogen atom in aryl halide, solvent, alkyl in (trialkylsilyl)acetylenes, and catalyst (Pd(0) *vs.* Pd(0)/Cu(I)), the target products can be obtained in good or excellent yields.

EXPERIMENTAL

General. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were measured at 500 or 200 MHz, ^{13}C NMR spectra at 125 MHz, in $CDCl_3$ with TMS as an internal standard, in acetone-d_6 (referenced to acetone), and in dimethyl sulfoxide-d_6 (referenced to dimethyl sulfoxide). HMBC experiments were setup for $J_{C\text{-}H}$=5 Hz. IR spectra were measured in $CHCl_3$, CCl_4, and in KBr pellets. EI MS spectra were determined at an ionizing voltage 70 eV. FAB MS spectra were measured using the thioglycerol/glycerol matrix and methanol as a solvent. HR MS spectra were obtained by the EI or FAB technique. All reactions were performed in Schlenk or double-necked flasks equipped with rubber septa and connected *via* rubber tubings to a standard vacuum/argon line. All chemicals were reagent grade materials. Tetrahydrofuran was freshly distilled from sodium/benzophenone under nitrogen; diisopropylamine, piperidine, and 2,2,6,6-tetramethylpiperidine were distilled from calcium hydride under argon and degassed by three freeze-pump-thaw cycles before use, dimethylformamide was distilled from calcium hydride under reduced pressure and stored over 4Å molecular sieves, methanol was distilled with sodium and stored over 4Å molecular sieves. The reactions with gaseous acetylene under 1 atm pressure were performed in a vessel connected to a rubber balloon filled with acetylene directly from a cylinder. Bubbling of gaseous acetylene (purified by passing through a dry-ice trap, concentrated sulfuric acid, and potassium hydroxide pellets) into the reaction mixture led to reduced yields of coupled products. (Trimethylsilyl)- and (triisopropylsilyl)acetylene (Aldrich) were used as received. The starting aryl halides were purchased from Aldrich (**3**), Acros (**5**), and Avocado (**21**) or prepared according to the literature procedures (**4**[17], **15**[18], and **18**[18]). The novel or modified syntheses of starting aryl halides **6**, **11**, and **22**[19] or acetylenes **23**, **24**, and **25**[20] are reported in *Experimental* (see below). TLC was performed on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by ceric sulfate/phosphomolybdic acid/sulfuric acid solution. Flash chromatography was performed on Silpearl silica gel (Kavalier Votice, Czech Republic) or Silica gel 60 (0.040-0.063 mm or <0.063 mm, Merck). Semipreparative HPLC was carried out on a silica gel column (Partisil M9, Whatman 10/50, 500 mm x 10 mm; sample injections on a 10-20 mg scale) using a refractometric detector.

General Procedure for the Coupling Reaction of Aryl Halides 3-6, 11 with Gaseous Acetylene

Method A. A Schlenk flask was charged with aryl halide (5.0 mmol), $Pd(PPh_3)_4$ (1-5 mol%), CuI (2-10 mol%), stoppered with a rubber septum, and flushed with argon. Piperidine (10 mL) was added and the mixture was briefly heated at 40-50 °C under stirring to get a clear solution. Then a rubber balloon filled with acetylene was attached to the side arm and the flask was purged of remaining argon using a needle introduced through the septum over the surface of the reaction medium. The mixture was stirred under 1 atm pressure of acetylene at 25-80 °C for 0.3-20 h until the educt disappeared (monitored by TLC). The precipitate was filtered off and washed with petroleum ether (2 x 5 mL). The combined fractions were evaporated to dryness *in vacuo* (at <50 °C) and the residue was chromatographed on silica gel to obtain the product.

Method B. It differs from the Method A in the absence of CuI.

General Procedure for the Coupling Reaction of Aryl Halides 6, 11, 15, 18 with (Trimethylsilyl)-acetylene

Method C. A glass pressure tube with gas inlet was charged with aryl halide (1.0 mmol) and $Pd(PPh_3)_4$ (58 mg, 5 mol%). The tube was stoppered with a rubber septum and flushed with argon. Piperidine (or diisopropylamine; 3 mL) was added and the mixture was briefly heated under stirring at 40-50 °C to get a clear solution. After cooling to rt, (trimethylsilyl)acetylene (310 μL, 2.2 equiv) was added. The septum was replaced in a stream of argon with a needle valve which was tightly closed. The reaction mixture was stirred at 80 °C for 2.5-12 h until the educt disappeared (monitored by TLC). The precipitate was filtered off and washed with petroleum ether (2 x 2 mL). The combined fractions were evaporated to dryness *in vacuo* (at <50 °C) and the residue was chromatographed on silica gel to obtain the product.

General Procedure for the Coupling Reaction of Aryl Halides 6, 11, 15, 18 with (Triisopropylsilyl)-acetylene

Method D. A Schlenk flask was charged with aryl halide (1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 5 mol%), and flushed with argon. Piperidine (diisopropylamine or 2,2,6,6-tetramethylpiperidine; 3 mL) was added and the mixture was briefly heated under stirring at 40-50 °C to get a clear solution. (Triisopropylsilyl)acetylene (270 μL, 1.2 equiv) was added and the reaction mixture was stirred at 80 °C for 17-50 h until the educt disappeared (monitored by TLC). The precipitate was filtered off and washed with petroleum ether (2 x 2 mL). The combined fractions were evaporated to dryness *in vacuo* (at <50 °C) and the residue was chromatographed on silica gel to obtain the product.

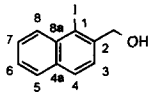
General Procedure for the Coupling Reaction of Aryl Halides (6, 15, 18, 21, 22) with Aryl Acetylenes (23-25)

Method E. A Schlenk flask was charged with aryl halide (1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 5 mol%), CuI (20 mg, 10 mol%) and flushed with argon. Piperidine (or diisopropylamine; 2 mL) was added and the mixture

was briefly heated under stirring at 40-50 °C to get a clear solution. Aryl acetylene (1.0 mmol) in piperidine (or diisopropylamine; 1 mL) was added and the reaction mixture was stirred at 25-80 °C for 1-50 h until the educt disappeared (monitored by TLC). The precipitate was filtered off and washed with petroleum ether (2 x 2 mL). The combined fractions were evaporated to dryness *in vacuo* (at <50 °C) and the residue was chromatographed on silica gel to obtain the product.

Method F. It differs from the Method E in the absence of CuI.

1-Iodo-2-naphthylmethanol 6



1-bromo-2-naphthylmethanol **15**[18] (4.04 g, 17.06 mmol) in dry tetrahydrofuran (50 mL) was treated under argon with n-butyllithium (24.0 mL of a 1.6 M solution in hexanes, 38.40 mmol, 2.3 equiv) at –78 °C for 10 min. A solution of iodine (10.80 g, 42.55 mmol, 2.5 equiv) in dry tetrahydrofuran (40 mL) was added. The reaction mixture was stirred at –78 °C for 10 min and then allowed to warm up to rt. The solvents were removed *in vacuo*. The residue was dissolved in dichloromethane and the solution was washed with water (1 x), 5 % aq $Na_2S_2O_3$ (3 x), and dried over anhydrous Na_2SO_4. After evaporation of dichloromethane, the crude product was purified by flash chromatography on silica gel (petroleum ether-ether-acetone 80:10:10 to 75:10:15) to obtain **6** (4.51 g, 93 %).

Mp: 102-103 °C (petroleum ether-acetone).

^{1}H NMR (500 MHz, $CDCl_3$): 2.18 (1 H, t, J=6.5 Hz, OH), 4.95 (2 H, d, J=6.1 Hz, CH_2), 7.51 (1 H, ddd, J=8.1, 6.8, 1.2 Hz, 6-H), 7.58 (1 H, ddd, J=8.6, 6.8, 1.3 Hz, 7-H), 7.60 (1 H, d, J=8.3 Hz, 3-H), 7.78 (1 H, dd, J=8.1, 1.3 Hz, 5-H), 7.83 (1 H, d, J=8.3 Hz, 4-H), 8.22 (1 H, bd, J=8.6 Hz, 8-H).

^{13}C NMR (125 MHz, $CDCl_3$): 70.96 (t, CH_2), 102.97 (s, C-1), 125.94 (d, C-3), 126.58 (d, C-8), 127.87 (d, C-6, C-7), 129.11 (d, C-5), 132.21 (d, C-4), 133.74 (s, C-4a), 134.70 (s, C-8a), 141.89 (s, C-2).

IR ($CHCl_3$): 3610 m, 3464 w, 3059 w, 1621 vw, 1595 vw, 1552 w, 1502 m, 1258 m, 1059 m, 1033 m, 863 w, 817 vs cm^{-1}.

FAB MS (m/z): 284 (M^+), 266, 181, 141, 128, 115, 93, 73, 57.

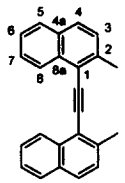
HR FAB MS: calcd for $C_{11}H_9IO$ 283.9698, found 283.9690.

1,2-Di(2-methylphenyl)acetylene 7[10a]

Method A: **3** (9.0 mL, 70.71 mmol), $Pd(PPh_3)_4$ (1.23 g, 1.06 mmol, 1.5 mol%), CuI (404 mg, 2.12 mmol, 3 mol%), piperidine (100 mL), gaseous acetylene, 80 °C, 15 min. Flash chromatography on silica gel (petroleum ether) afforded **7** as an oil (6.98 g, 96 %).

^{1}H NMR (200 MHz, $CDCl_3$) in accord with the literature data.[10b]

1,2-Di(2-methyl-1-naphthyl)acetylene 8[11]



Method A: **4**[17] (4.11 g, 15.33 mmol), $Pd(PPh_3)_4$ (880 mg, 0.76 mmol, 5 mol%), CuI (297 mg, 1.56 mmol, 10 mol%), piperidine (25 mL), gaseous acetylene, 80 °C, 1.5 h. Flash chromatography on silica gel (petroleum ether-ether 97:3 to 94:6) afforded **8** (1.90 g, 81 %).

Mp in accord with the literature data.[11]

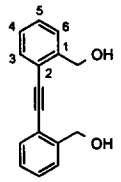
^{1}H NMR (500 MHz, $CDCl_3$): 2.83 (6 H, s, CH_3), 7.41 (2 H, d, J=8.3 Hz, 3-H), 7.47 (2 H, ddd, J= 8.1, 6.9, 1.2 Hz, 6-H), 7.59 (2 H, ddd, J=8.2, 6.9, 1.2 Hz, 7-H), 7.75 (2 H, d, J=8.3 Hz, 4-H), 7.83 (2 H, dd, J=8.1, 0.9 Hz, 5-H), 8.60 (2 H, dq, J=8.3, 1.0, 1.0, 1.0 Hz, 8-H).

^{13}C NMR (125 MHz, $CDCl_3$): 21.93 (q, CH_3), 95.87 (s, -C≡), 119.93 (s, C-1), 125.49 (d, C-3), 126.01 (d, C-8), 126.91 (d, C-6), 128.16 (d, C-7), 128.18 (d, C-4, C-5), 131.71 (s, C-4a), 133.61 (s, C-8a), 139.07 (s, C-2).

IR (CCl_4): 3057 vs, 3012 m, 2950 m, 1623 w, 1592 m, 1570 m, 1509 vs, 1399 s, 1378 m, 1276 w, 1212 w, 1203 w, 1155 w, 1144 w, 1097 w, 1027 m, 865 m cm^{-1}.

EI MS (m/z, rel. intensity): 306 ($M^{+\cdot}$, 100), 288 (32), 276 (18), 144 (13), 85 (12), 71 (17), 57 (25).

2-[2-(2-Hydroxymethylphenyl)-1-ethynyl]phenylmethanol 9[12]



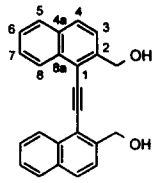
Method A: **5** (3.0 g, 12.82 mmol), $Pd(PPh_3)_4$ (161 mg, 0.14 mmol, 1 mol%), CuI (55 mg, 0.29 mmol, 2 mol%), piperidine (10 mL), gaseous acetylene, rt, 1 h. Flash chromatography on silica gel (petroleum ether-ether 80:20 to 50:50) afforded **9** (1.44 g, 94 %). Crystallization from acetone provided 1.11 g of **9** (73 %).

Mp, ^{1}H NMR (500 MHz, acetone-d_6), and IR (KBr) in accord with the literature data.[12]

^{13}C NMR (125 MHz, acetone-d_6): 63.25 (t, CH_2), 92.31 (s, -C≡), 121.68 (s, C-2), 127.56 (d, C-4), 127.68 (d, C-6), 129.50 (d, C-5), 132.61 (d, C-3), 144.86 (s, C-1).

EI MS (m/z, rel. intensity): 238 ($M^{+\cdot}$, 21), 220 (73), 202 (10), 191 (100), 178 (24), 165 (40), 152 (14), 119 (32), 115 (16), 95 (14), 91 (20), 77 (19), 63 (10).

1-[2-(2-Hydroxymethyl-1-naphthyl)-1-ethynyl]-2-naphthylmethanol 10



Method E: **6** (1.15 g, 4.05 mmol), **23** (738 mg, 4.05 mmol), $Pd(PPh_3)_4$ (234 mg, 0.20 mmol, 5 mol%), CuI (77 mg, 0.40 mmol, 10 mol%), piperidine (45 mL), 40 °C, 20 h. Flash chromatography on silica gel (petroleum ether-ether-acetone-methanol 70:15:15:0 gradually to 0:0:0:100) afforded **10** (1.06 g, 77 %).

Mp: 213-215 °C (methanol).

^{1}H NMR (500 MHz, dimethyl sulfoxide-d_6, 40 °C): 5.10 (4 H, bs, CH_2), 5.51 (2 H, bs, OH), 7.61 (2 H, ddd, J=8.0, 6.8, 1.2 Hz, 6-H), 7.73 (2 H, ddd, J=8.3, 6.8, 1.3 Hz, 7-H), 7.83 (2 H, d, J=8.5 Hz, 3-H), 8.03 (2 H, bd, J=8.1 Hz, 5-H), 8.05 (2 H, d, J=8.5 Hz, 4-H), 8.52 (2 H, bd, J=8.3 Hz, 8-H).

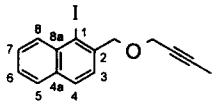
^{13}C NMR (125 MHz, dimethyl sulfoxide-d_6, 40 °C): 61.96 (t, CH_2), 94.82 (s, -C≡), 116.29 (s, C-1), 124.83 (d, C-3), 125.14 (d, C-8), 126.16 (d, C-7), 127.43 (d, C-6), 128.43 (d, C-5), 128.78 (d, C-4), 131.90 (s, C-4a), 132.44 (s, C-8a), 143.35 (s, C-2).

IR (KBr): 3266 s, 3170 m (sh), 3055 m, 3011 w, 1591 w, 1570 w, 1508 m, 1064 m, 1060 vs, 1025 w, 859 w, 814 s cm^{-1}.

EI MS (m/z, rel. intensity): 338 ($M^{+\cdot}$, 9), 320 (100), 302 (13), 291 (58), 277 (63), 265 (12), 201 (9), 169 (14), 154 (17), 138 (19), 127 (12), 97 (8), 69 (11), 57 18), 43 (13).

HR EI MS: calcd for $C_{24}H_{18}O_2$ 338.1307, found 338.1303.

2-(2-Butynyloxymethyl)-1-iodonaphthalene 11



A solution of **6** (1.97 g, 6.94 mmol) in dry dimethylformamide (18 mL) was added at 0 °C to a suspension of sodium hydride (305 mg of a 80 % suspension in mineral oil, 10.17 mmol, 1.5 equiv) in dry dimethylformamide (4 mL) under argon. The mixture was stirred at 0 °C for 1.5 h. 1-Bromo-2-butyne (910 μL, 10.48 mmol, 1.5 equiv) was added and the reaction was allowed to reach rt within 2 h while stirred. The mixture was carefully diluted with water and extracted with ether (3 x). Combined organic portions were washed with water (1 x) and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 90:10) to afford **11** as an oil (2.25 g, 96 %).

^{1}H NMR (500 MHz, $CDCl_3$): 1.89 (3 H, t, J=2.3 Hz, CH_3), 4.27 (2 H, q, J=2.3 Hz, -CH_2-C≡), 4.86 (2 H, s, -CH_2-Nph), 7.50 (1 H, ddd, J=8.0, 6.8, 1.2 Hz, 6-H), 7.56 (1 H, ddd, J=8.4, 6.8, 1.3 Hz, 7-H), 7.59

(1 H, d, J=8.4 Hz, 3-H), 7.77 (1 H, dd, J=8.1, 1.6 Hz, 5-H), 7.81 (1 H, d, J=8.5 Hz, 4-H), 8.24 (1 H, dq, J=8.5, 0.9, 0.9, 0.9 Hz, 8-H).

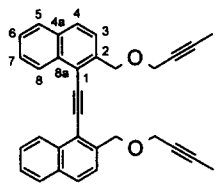
^{13}C NMR (125 MHz, $CDCl_3$): 3.79 (q, CH_3), 58.58 (t, -$\underline{C}H_2$-C≡), 75.05 (s, ≡$\underline{C}$-CH_3), 77.37 (t, -CH_2-Nph), 83.21 (s, ≡$\underline{C}$-CH_2-), 103.53 (s, C-1), 126.27 (d, C-3), 126.64 (d, C-6), 127.84 (d, C-5), 128.42 (d, C-4), 128.90 (d, C-7), 132.45 (d, C-8), 133.85 (s, C-4a), 134.81 (s, C-8a), 139.66 (s, C-2).

IR ($CHCl_3$): 3059 m, 3011 s, 2949 m, 2923 m, 2856 m, 2242 w, 2225 w, 1621 w, 1595 w, 1552 m, 1502 s, 1425 m, 1387 m, 1355 s, 1257 s, 1138 s, 1095 vs, 1072 vs, 1022 m, 863 m, 816 vs, 523 s, 422 w cm^{-1}.

EI MS (m/z, rel. intensity): 336 ($M^{+\cdot}$, 27), 282 (37), 267 (21), 253 (6), 179 (100), 165 (9), 154 (11), 141 (64), 126 (38), 115 (7), 83 (7), 69 (13).

HR EI MS: calcd for $C_{15}H_{13}IO$ 336.0011, found 336.0004.

2-(2-Butynyloxymethyl)-1-{2-[2-(2-butynyloxymethyl)-1-naphthyl]-1-ethynyl}naphthalene 12



Method A: **11** (75 mg, 0.22 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol, 5 mol%), CuI (4 mg, 0.021 mmol, 10 mol%), piperidine (2 mL), gaseous acetylene, 80 °C, 1 h. Flash chromatography on silica gel (petroleum ether-ether 90:10) afforded **12** (24 mg, 49 %).

Mp: 115-116 °C (petroleum ether-ether).

^{1}H NMR (500 MHz, $CDCl_3$): 1.73 (6 H, t, J=2.3 Hz, CH_3), 4.29 (4 H, q, J=2.3 Hz, -CH_2-C≡), 5.18 (4 H, s, -CH_2-Nph), 7.55 (2 H, ddd, J=8.2, 6.8, 1.2 Hz, 7-H), 7.64 (2 H, ddd, J=8.2, 6.7, 1.3 Hz, 6-H), 7.73 (2 H, d, J=8.5 Hz, 3-H), 7.89 (2 H, bd, J=8.2 Hz, 5-H), 7.90 (2 H, bd, J=8.5 Hz, 4-H), 8.61 (2 H, bd, J=8.3 Hz, 8-H).

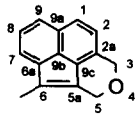
^{13}C NMR (125 MHz, $CDCl_3$): 3.49 (q, CH_3), 58.39 (t, -$\underline{C}H_2$-C≡), 70.33 (t, -CH_2-Nph), 75.10 (s, ≡$\underline{C}$-CH_3), 82.94 (s, ≡$\underline{C}$-CH_2-), 95.07 (s, ≡C-Nph), 119.29 (s, C-1), 125.60 (d, C-3), 126.40 (d, C-6, C-8), 127.15 (d, C-7), 128.28 (d, C-5), 128.89 (d, C-4), 132.73 (s, C-4a), 133.42 (s, C-8a), 138.70 (s, C-2).

IR (CCl_4): 3060 w, 3010 vw, 2956 m, 2922 w, 2855 m, 2251 vw, 2225 vw, 1621 w, 1593 w, 1572 w, 1509 w, 1399 w, 1380 w, 1356 m, 1262 w, 1138 m, 1077 m, 1024 w, 865 w, 820 m, 761 vs, 428 w cm^{-1}.

EI MS (m/z, rel. intensity): 442 ($M^{+\cdot}$, 25), 388 (26), 359 (17), 335 (38), 319 (100), 304 (32), 289 (67), 276 (43), 141 (14), 97 (19), 71 (33), 57 (42), 43 (38).

HR EI MS: calcd for $C_{32}H_{26}O_2$ 442.1933, found 442.1948.

6-Methyl-3,5-dihydroindeno[2,1,7-*def*]isochromene 13



A mixture of **11** (136 mg, 0.41 mmol) and $Pd(PPh_3)_4$ (24 mg, 0.021 mmol, 5 mol%) in piperidine (2 mL) was stirred under argon at 80 °C for 40 h. The solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel (petroleum ether-ether 90:10) to obtain **13** as an oil (34 mg, 41 %) and unreacted **11** (32 mg, 23 % recovery).

^{1}H NMR (500 MHz, $CDCl_3$): 2.27 (3 H, t, J=1.4 Hz, CH_3), 4.84 (2 H, s, 3-H), 4.92 (2 H, q, J=1.4 Hz, 5-H), 7.21 (1 H, d, J=8.3 Hz, 2-H), 7.47 (1 H, dd, J=8.1, 6.7 Hz, 8-H), 7.56 (1 H, d, J=6.7 Hz, 7-H), 7.62 (1 H, d, J=8.3 Hz, 1-H), 7.68 (1 H, d, J=8.1 Hz, 9-H).

^{13}C NMR (125 MHz, $CDCl_3$): 10.99 (q, CH_3), 64.84 (t, C-5), 65.42 (t, C-3), 122.17 (d, C-7), 123.12 (d, C-8), 125.91 (d, C-1), 126.29 (d, C-9), 126.41 (s, C-6), 126.82 (s, C-9b), 127.69 (s, C-5a), 128.03 (d, C-2), 130.74 (s, C-9a), 131.72 (s, C-2a), 134.48 (s, C-6a), 142.35 (s, C-9c).

IR ($CHCl_3$): 3052 m, 1668 w, 1628 w, 1599 w, 1578 w, 1486 s, 1468 m, 1444 s, 1430 s, 1380 w (sh), 1362 s, 1351 m, 1331 m, 1199 m, 1180 w, 1137 m, 1047 s, 1038 s, 1027 s, 952 m, 883 s, 856 s, 822 s cm^{-1}.

EI MS (m/z, rel. intensity): 208 ($M^{+\cdot}$, 62), 193 (10), 179 (74), 165 (100), 152 (17), 111 (6), 97 (8), 81 (10), 69 (17), 57 (13), 43 (11).

HR EI MS: calcd for $C_{15}H_{12}O$ 208.0888, found 208.0889.

2-[2-(2-Butynyloxymethyl)-1-naphthyl]-1-ethynyl(trimethyl)silane 14a

Method C: **11** (88 mg, 0.26 mmol), $Pd(PPh_3)_4$ (17 mg, 0.014 mmol, 5 mol%), (trimethylsilyl)-acetylene (90 μL, 0.61 mmol, 2.3 equiv), piperidine (2 mL), 80 °C, 3 h. Flash chromatography on silica gel (petroleum ether-ether-acetone 96:2:2 to 90:10:0) afforded **14a** as an oil (12 mg, 15 %) and **13** as an oil (6 mg, 11 %).

^{1}H NMR (500 MHz, $CDCl_3$): 0.35 (9 H, s, $(CH_3)_3Si$-), 1.88 (3 H, t, J=2.3 Hz, CH_3), 4.22 (2 H, q, J=2.3 Hz, -CH_2-C≡), 4.97 (2 H, s, -CH_2-Nph), 7.49 (1 H, ddd, J=8.2, 6.8, 1.3 Hz, 6-H), 7.57 (1 H, ddd, J=8.4, 6.8, 1.3 Hz, 7-H), 7.61 (1 H, d, J=8.4 Hz, 3-H), 7.81 (1 H, bddd, J=8.2, 1.3, 0.8 Hz, 5-H), 7.82 (1 H, bd, J=8.4 Hz, 4-H), 8.34 (1 H, ddt, J=8.4, 1.2, 0.8, 0.8 Hz, 8-H).

^{13}C NMR (125 MHz, $CDCl_3$): 0.09 (q, $(CH_3)_3Si$-), 3.43 (q, CH_3), 58.38 (t, -$\underline{C}H_2$-C≡), 70.12 (t, -CH_2-Nph), 75.20 (s, ≡$\underline{C}$-CH_3), 82.56 (s, ≡$\underline{C}$-CH_2-), 100.48 (s, ≡C-Si), 105.06 (s, ≡C-Nph), 119.01 (s, C-1),

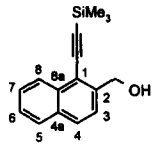
125.31 (d, C-3), 126.27 (d, C-8), 126.29 (d, C-6), 126.95 (d, C-7), 128.10 (d, C-5), 128.76 (d, C-4), 132.50 (s, C-4a), 133.33 (s, C-8a), 139.13 (s, C-2).

IR ($CHCl_3$): 3061 w, 2924 w, 2900 w, 2857 w, 2242 vw, 2224 vw, 2148 w, 1594 vw, 1569 vw, 1508 w, 1408 w, 1376 w, 1356 w, 1331 w, 1251 s, 1261 w (sh), 1155 w, 1138 w, 1095 m (sh), 1082 m, 1066 m, 953 w, 908 vw, 872 s, 846 vs, 822 m, 701 w, 643 w cm^{-1}.

EI MS (m/z, rel. intensity): 306 ($M^{+\cdot}$, 6), 291 (7), 252 (14), 238 (12), 233 (9), 179 (8), 165 (8), 97 (4), 73 (100).

HR EI MS: calcd for $C_{20}H_{22}OSi$ 306.1440, found 306.1453.

1-(2-Trimethylsilyl-1-ethynyl)-2-naphthylmethanol 16a



Method C: **15** (95 mg, 0.40 mmol), (trimethylsilyl)acetylene (125 μL, 0.88 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (23 mg, 0.020 mmol, 5 mol%), piperidine (2 mL), 80 °C, 12 h. Flash chromatography on silica gel (petroleum ether-ether-acetone 95:5:0 to 80:10:10) afforded a fraction of lipophilic products (66 mg) and unreacted **15** (19 mg, 20 % recovery). Compounds **16a** and **17** contained in the lipophilic fraction were separated by semipreparative HPLC on a silica gel column (petroleum ether-acetone 95:5) to provide **17** as an oil (11 mg, 8 %) and more polar **16a** as an oil (25 mg, 25 %).

^1H NMR (500 MHz, $CDCl_3$): 0.35 (9 H, s, $(CH_3)_3Si$-), 5.03 (2 H, s, CH_2), 7.50 (1 H, ddd, J=8.1, 6.8, 1.2 Hz, 7-H), 7.58 (1 H, d, J=8.3 Hz, 3-H), 7.58 (1 H, ddd, J=8.3, 6.8, 1.2 Hz, 6-H), 7.84 (1 H, bd, J=8.3 Hz, 4-H), 7.84 (1 H, bd, J=8.1 Hz, 8-H), 8.34 (1 H, dq, J=8.5, 1.1, 1.1, 1.1 Hz, 5-H).

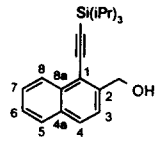
^{13}C NMR (125 MHz, $CDCl_3$): 0.04 (q, $(CH_3)Si$-), 64.43 (t, CH_2), 100.51 (s, ≡C-Si), 105.44 (s, ≡C-Nph), 118.27 (s, C-1), 125.14 (d, C-6), 126.13 (d, C-7), 126.33 (d, C-5), 127.13 (d, C-4), 128.17 (d, C-8), 129.05 (d, C-3), 132.51 (s, C-4a), 133.47 (s, C-8a), 142.11 (s, C-2).

IR ($CHCl_3$): 3608 w, 3061 w, 2962 w, 2900 w, 2142 w, 1602 w, 1594 w, 1569 vw, 1507 w, 1262 w, 1252 m, 1027 w, 872 s, 847 vs, 822 m, 642 w cm^{-1}.

EI MS (m/z, rel. intensity): 254 ($M^{+\cdot}$, 100), 239 (16), 221 (19), 181 (37), 179 (48), 165 (29), 139 (6), 112 (20), 99 (8), 73 (63), 61 (18).

HR EI MS: calcd for $C_{16}H_{18}OSi$ 254.1126, found 254.1138.

1-(2-Triisopropylsilyl-1-ethynyl)-2-naphthylmethanol 16b



Method D: **6** (4.0 g, 14.08 mmol), (triisopropylsilyl)acetylene (3.80 mL, 16.94 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (814 mg, 0.70 mmol, 5 mol%), diisopropylamine (80 mL), 80 °C, 40 h. Flash chromatography on silica gel (petroleum ether-ether 95:5 to 85:15) afforded **16b** as an oil (4.58 g, 96 %).

^{1}H NMR (500 MHz, $CDCl_3$): 1.21 (21 H, m, ΣJ=7.1 Hz, $(CH_3)_2CH$-), 5.06 (2 H, s, CH_2), 7.50 (1 H, ddd, J=8.0, 6.8, 1.2 Hz, 6-H), 7.58 (1 H, ddd, J=8.3, 6.9, 1.2 Hz, 7-H), 7.59 (1 H, d, J=8.3 Hz, 3-H), 7.83 (1 H, d, J=8.3 Hz, 4-H), 7.83 (1 H, bdd, J=8.0, 1.0 Hz, 5-H), 8.39 (1 H, ddt, J=8.3, 1.0, 0.9, 0.9 Hz, 8-H).

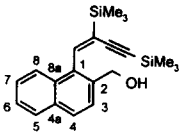
^{13}C NMR (125 MHz, $CDCl_3$): 11.35 (d, CH-Si), 18.76 (q, CH_3), 64.50 (t, CH_2), 102.02 (s, ≡C-Si), 102.21 (s, ≡C-Nph), 118.54 (s, C-1), 125.07 (d, C-3), 126.12 (d, C-8), 126.28 (d, C-6), 127.13 (d, C-7), 128.19 (d, C-5), 128.88 (d, C-4), 132.49 (s, C-4a), 133.61 (s, C-8a), 142.12 (s, C-2).

IR ($CHCl_3$): 3607 w, 3061 w, 3012 m, 2959 s, 2945 vs, 2866 vs, 2142 w, 1593 w, 1567 w, 1508 w, 1463 m, 1383 m, 1368 w, 1268 w, 1074 m, 1027 m, 1017 m, 1013 m, 996 m, 883 s, 868 m, 822 s, 638 m cm^{-1}.

EI MS (m/z, rel. intensity): 338 ($M^{+\cdot}$, 59), 295 (14), 277 (23), 253 (30), 235 (29), 225 (100), 207 (16), 193 (20), 165 (33), 112 (18), 61 (15).

HR EI MS: calcd for $C_{22}H_{30}OSi$ 338.2066, found 338.2062.

1-[(E)-2,4-Di(trimethylsilyl)-1-buten-3-ynyl]-2-naphthylmethanol 17



For preparation, see **16a**.

^{1}H NMR (500 MHz, $CDCl_3$): -0.04 (9 H, s, $(CH_3)_3Si$-C≡), 0.34 (9 H, s, $(CH_3)_3Si$-C=), 2.47 (1 H, t, J=6.5 Hz, OH), 4.76 (2 H, d, J=6.5 Hz, CH_2), 7.41 (1 H, s, -HC=), 7.47-7.49 (2 H, m, 6-H, 7-H), 7.66 (1 H, d, J=8.3 Hz, 3-H), 7.81-7.86 (2 H, m, 5-H, 8-H), 7.83 (1 H, d, J=8.3 Hz, 4-H).

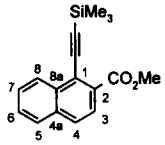
^{13}C NMR (125 MHz, $CDCl_3$): -1.84 (q, $(\underline{C}H_3)_3Si$-C=), -0.33 (q, , $(\underline{C}H_3)_3Si$-C≡), 64.06 (t, CH_2), 104.51 (s, ≡C-Si), 105.51 (s, -$\underline{C}$≡C-Si), 125.44 (d, C-6), 125.82 (d, C-7), 126.01 (d, C-8), 127.12 (d, C-3), 128.16 (d, C-4, C-5), 131.09 (s, C-4a), 131.98 (s, =C-Si), 132.84 (s, C-8a), 133.98 (s, C-2), 135.52 (s, C-1), 145.12 (d, -CH=).

IR ($CHCl_3$): 3609 w, 3518 w, 2960 m, 2898 w, 2117 m, 1597 w, 1569 w, 1507 w, 1407 w, 1251 s, 1029 w, 881 s, 858 vs, 845 vs, 825 m, 633 m, 542 w cm^{-1}.

EI MS (m/z, rel. intensity): 352 ($M^{+\cdot}$, 28), 279 (64), 262 (22), 249 (39), 235 (7), 219 (10), 189 (14), 182 (21), 169 (12), 147 (10), 73 (100), 45 (16).

HR EI MS: calcd for $C_{21}H_{28}OSi_2$ 352.1679, found 352.1666.

Methyl 1-(2-Trimethylsilyl-1-ethynyl)-2-naphthoate 19a



Method C: **18** (210 mg, 0.79 mmol), (trimethylsilyl)acetylene (250 μL, 1.77 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (46 mg, 0.040 mmol, 5 mol%), piperidine (2 mL), 80 °C, 10 h. Flash chromatography on silica gel (petroleum ether-ether 95:5) afforded a fraction of two products. Separation of them was accomplished by semipreparative HPLC on a silica gel column (petroleum ether-acetone 95:5) to provide **20** as an oil (41 mg, 19 %) and more polar **19a** as an oil (60 mg, 27 %).

^{1}H NMR (500 MHz, $CDCl_3$): 0.37 (9 H, s, $(CH_3)_3Si$-), 3.99 (3 H, s, CH_3O-), 7.60 (1 H, ddd, J=8.3, 6.9, 1.5 Hz, 6-H), 7.63 (1 H, ddd, J=8.3, 6.9, 1.5 Hz, 7-H), 7.83 (1 H, d, J=8.6 Hz, 4-H), 7.85 (1 H, dd, J=8.6, 1.6 Hz, 5-H), 7.92 (1 H, d, J=8.6 Hz, 3-H), 8.55 (1 H, bd, J=8.3 Hz, 8-H).

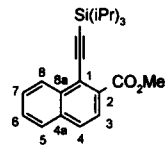
^{13}C NMR (125 MHz, $CDCl_3$): -0.03 (q, $(CH_3)_3Si$-), 52.13 (q, CH_3O-), 100.70 (s, ≡C-Si), 106.78 (s, ≡C-Nph), 121.79 (s, C-1), 125.65 (d, C-3), 127.57 (d, C-4), 127.70 (d, C-5), 128.12 (d, C-7, C-8), 128.46 (d, C-6), 131.31 (s, C-8a), 134.37 (s, C-4a), 167.55 (s, C=O).

IR ($CHCl_3$): 3063 w, 2901 w, 2152 w, 1718 s, 1620 vw, 1593 w, 1564 w, 1506 vw, 1462 m, 1436 m, 1281 m, 1250 s, 877 m, 867 m, 846 vs cm^{-1}.

EI MS (m/z, rel. intensity): 282 ($M^{+\cdot}$, 79), 267 (42), 251 (12), 237 (100), 193 (12), 165 (23), 111 (12), 59 (3).

HR EI MS: calcd for $C_{17}H_{18}O_2Si$ 282.1076, found 282.1069.

Methyl 1-(2-Triisopropylsilyl-1-ethynyl)-2-naphthoate 19b



Method D: **18** (46 mg, 0.17 mmol), (triisopropylsilyl)acetylene (85 μL, 0.38 mmol, 2.2 equiv), $Pd(PPh_3)_4$ (10 mg, 0.0087 mmol, 5 mol%), 2,2,6,6-tetramethylpiperidine (1 mL), 80 °C, 14 h. The reaction mixture was diluted with ether, washed with the saturated aqueous solution of $CuSO_4$ (3 x), 5 % aq $KHCO_3$ (2 x), water (1 x), and dried over anhydrous Na_2SO_4. Flash chromatography on silica gel (petroleum ether-ether 95:5) afforded **19b** as an oil (43 mg, 67 %).

^{1}H NMR (500 MHz, $CDCl_3$): 1.22 (21 H, m, ΣJ=9.8 Hz, $(CH_3)_2CH$-), 3.97 (3 H, s, CH_3O-), 7.59 (1 H, ddd, J=8.0, 6.8, 1.2 Hz, 6-H), 7.62 (1 H, ddd, J=8.3, 6.8, 1.5 Hz, 7-H), 7.82 (1 H, bd, J=8.5 Hz, 4-H), 7.85 (1 H, bdd, J=7.6, 1.8 Hz, 5-H), 7.88 (1 H, d, J=8.5 Hz, 3-H), 8.62 (1 H, bd, J=8.5 Hz, 8-H).

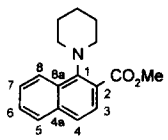
^{13}C NMR (125 MHz, $CDCl_3$): 11.42 (d, CH-Si), 18.72 (q, CH_3), 52.34 (q, CH_3O-), 102.28 (s, ≡C-Si), 103.48 (s, ≡C-Nph), 121.77 (s, C-1), 125.60 (d, C-3), 127.51 (d, C-4), 127.68 (d, C-5), 127.98 (d, C-7), 128.14 (d, C-8), 128.28 (d, C-6), 131.60 (s, C-8a), 133.84 (s, C-2), 134.30 (s, C-4a), 167.84 (s, C=O).

IR (CCl_4): 3063 m, 2945 vs, 2866 vs, 2150 m, 1736 vs, 1717 vs, 1621 w, 1593 m, 1565 m, 1505 w, 1462 vs, 1435 s, 1383 m, 1368 m (sh), 1243 vs, 1155 s, 1065 s, 996 s, 883 s, 868 m, 831 m, 678 s, 663 s, 635 m (sh), 462 w cm^{-1}.

EI MS (m/z, rel. intensity): 366 ($M^{+\cdot}$, 5), 323 (100), 293 (27), 251 (10), 223 (12), 179 (9), 126 (15), 111 (6), 59 (6).

HR EI MS: calcd for $C_{23}H_{30}O_2Si$ 366.2015, found 366.2064.

Methyl 1-Piperidino-2-naphthoate 20



A solution of **18** (86 mg, 0.32 mmol) in piperidine (2 mL) under argon was heated at 80 °C for 24 h. The solvent was evaporated *in vacuo* to dryness and the residue was passed through a short column of silica gel (petroleum ether-ether 100:0 to 90:10) to afford **20** as an oil (36 mg, 41 %).

^{1}H NMR (500 MHz, $CDCl_3$): 1.55 (2 H, bs, -C<u>H</u>$_2$-CH_2-CH_2-N), 1.78 (4 H, bs, -CH_2-C<u>H</u>$_2$-CH_2-N), 3.18 (4 H, bt, J=5.0 Hz, -CH_2-CH_2-C<u>H</u>$_2$-N), 3.97 (3 H, s, CH_3), 7.50 (1 H, d, J=8.5 Hz, 3-H), 7.50-7.56 (2 H, m, 6-H, 7-H), 7.80 (1 H, bd, J=8.5 Hz, 4-H), 7.80 (1 H, m, ΣJ=13.7 Hz, 5-H), 8.35 (1 H, m, ΣJ=15.6 Hz, 8-H).

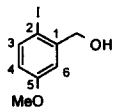
^{13}C NMR (125 MHz, $CDCl_3$): 24.54 (t, -<u>C</u>H_2-CH_2-CH_2-N), 26.98 (t, -CH_2-<u>C</u>H_2-CH_2-N), 52.29 (q, CH_3), 52.50 (t, -CH_2-CH_2-<u>C</u>H_2-N), 123.59 (d, C-3), 124.24 (s, C-2), 124.93 (d, C-8), 125.99 (d, C-5), 126.13 (d, C-7), 127.22 (d, C-4), 128.21 (d, C-6), 131.74 (s, C-8a), 135.80 (s, C-4a), 149.82 (s, C-1), 170.22 (s, C=O).

IR ($CHCl_3$): 3061 w, 2938 s, 2850 m, 1718 vs, 1620 w, 1596 w, 1565 m, 1503 w, 1463 m, 1452 m, 1441 m (sh), 1435 s, 1275 s, 870 w, 822 m cm^{-1}.

EI MS (m/z, rel. intensity): 269 ($M^{+\cdot}$, 65), 254 (100), 238 (34), 236 (16), 208 (16), 180 (10), 153 (11), 127 (26).

HR EI MS: calcd for $C_{17}H_{19}NO_2$ 269.1416, found 269.1407.

2-Iodo-5-methoxyphenylmethanol 22[19]



Dry methanol (80 mL) was cooled to –30 °C under nitrogen, thionylchloride (19.50 mL, 267.33 mmol, 4.0 equiv) was added under stirring and the solution was kept at –30 °C for 1 h. 2-Bromo-5-methoxybenzoic acid (15.30 g, 66.21 mmol) in dry methanol (100 mL) was added dropwise during a 45 min period. The mixture was stirred at –30 °C for additional 45 min and then it was heated at 40 °C for 18 h. The solvent was evaporated *in vacuo* and the residue was passed through a short column of alumina (petroleum ether-ether-acetone 80:10:10) to obtain methyl 2-bromo-5-methoxybenzoate (16.06 g, 99 %).

A suspension of $LiAlH_4$ (3.10 g, 81.69 mmol, 2.5 equiv) in dry THF (60 mL) was cooled to 0 °C under argon and a solution of methyl 2-bromo-5-methoxybenzoate (16.06 g, 65.53 mmol) in dry THF (30 mL) was added dropwise. The mixture was stirred at 0 °C for 40 min. Solid Na_2SO_4 was added and the excess of hydride was carefully decomposed with the saturated aqueous Na_2SO_4 solution. THF was removed *in vacuo*. The residue was extracted with ether (3 x), combined organic portions were washed with water (2 x) and dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* to afford the crude 2-bromo-5-methoxyphenylmethanol (13.80 g, 97 %).

n-Butyllithium (91.40 mL of a 1.6 M solution in hexanes, 146.24 mmol, 2.3 equiv) was added under argon at –78 °C to a solution of 2-bromo-5-methoxyphenylmethanol (13.80 g, 63.58 mmol; evaporated to dryness from a benzene solution) in dry THF (150 mL). The mixture was kept at –78 °C for 1 h. A solution of iodine (40.34 g, 158.94 mmol, 2.5 equiv) in dry THF (60 mL) was added and the mixture was stirred at –78 °C for 30 min and then it was allowed to warm up to rt. THF was evaporated *in vacuo* and the residue was triturated with dichloromethane. The solution was washed with 5 % aq $Na_2S_2O_3$ (3 x), water (1 x), dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo*. Flash chromatography on silica gel (petroleum ether-ether-acetone 90:10:0 to 80:10:10) afforded **22** (11.07 g, 66 %).

Mp in accord with the literature data.[19]

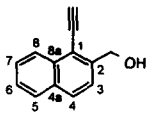
^1H NMR (500 MHz, $CDCl_3$): 3.81 (3 H, s, CH_3), 4.63 (2 H, s, CH_2), 6.60 (1 H, bdd, J=8.7, 3.1 Hz, 4-H), 7.07 (1 H, dt, J= 3.1, 0.7, 0.7 Hz, 6-H), 7.67 (1 H, d, J=8.7 Hz, 3-H).

^{13}C NMR (125 MHz, $CDCl_3$): 55.40 (q, CH_3), 69.19 (t, CH_2), 85.32 (s, C-2), 114.23 (d, C-6), 115.31 (d, C-4), 139.59 (d, C-3), 143.62 (s, C-1), 160.25 (s, C-5).

IR (CCl_4): 3610 m, 3468 w, 2839 m, 1589 s, 1570 s, 1466 vs, 1442 m, 1416 m, 1380 m, 1297 s, 1277 s, 1252 s, 1237 vs, 1191 m, 1162 s, 1129 m, 1048 s, 1006 s, 874 m, 858 m, 816 m, 805 m, 588 m, 561 w, 454 w, 440 w cm^{-1}.

EI MS (m/z, rel. intensity): 264 ($M^{+\cdot}$, 100), 218 (7), 135 (11), 109 (18), 94 (15), 77 (17), 63 (11), 50 (7), 39 (7).

1-(1-Ethynyl)-2-naphthylmethanol 23



n-Bu_4NF (6.50 mL of a 1 M solution in tetrahydrofuran, 6.50 mmol, 1.5 equiv) was added to **16b** (1.48 g, 4.37 mmol) in tetrahydrofuran (25 mL) and the mixture was stirred at rt for 30 min. The solvent was evaporated to dryness and the residue was chromatographed on silica gel (petroleum ether-ether-acetone 80:10:10 to 70:20:10) to get **23** (725 mg, 91 %).

Mp: 86-88 °C (petroleum ether-ether).

^{1}H NMR (500 MHz, $CDCl_3$): 3.76 (1 H, s, HC≡), 5.05 (2 H, s, CH_2), 7.51 (1 H, ddd, J=8.1, 6.8, 1.2 Hz, 6-H), 7.58 (1 H, ddd, J=8.3, 6.8, 1.5 Hz, 7-H), 7.61 (1 H, d, J=8.5 Hz, 3-H), 7.84 (1 H, bd, J=8.1 Hz, 5-H), 7.86 (1 H, d, J=8.5 Hz, 4-H), 8.37 (1 H, dq, J=8.3, 1.0, 1.0, 1.0 Hz, 8-H).

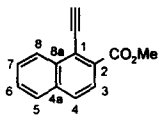
^{13}C NMR (125 MHz, $CDCl_3$): 64.18 (t, CH_2), 79.26 (s, ≡C-Nph), 87.33 (d, HC≡), 117.24 (s, C-1), 125.11 (d, C-3), 126.01 (d, C-8), 126.40 (d, C-7), 127.21 (d, C-6), 128.20 (d, C-5), 129.36 (d, C-4), 132.47 (s, C-4a), 133.64 (s, C-8a), 142.36 (s, C-2).

IR ($CHCl_3$): 3608 m, 3302 vs, 3062 w, 2884 w, 2099 w, 1623 vw, 1593 w, 1569 w, 1508 w, 1375 m, 1331 w, 1011 m, 822 vs, 659 s, 617 m cm^{-1}.

EI MS (m/z, rel. intensity): 182 ($M^{+\cdot}$, 69), 165 (11), 153 (100), 127 (7), 76 (14), 63 (10), 51 (8).

HR EI MS: calcd for $C_{13}H_{10}O$ 182.0732, found 182.0730.

Methyl 1-(1-Ethynyl)-2-naphthoate 24



Compound **19a** (272 mg, 0.96 mmol) in dry methanol (4 mL) was treated under argon with sodium methoxide (1.65 mmol, 1.7 equiv; 38 mg of sodium dissolved in 1.2 mL of dry methanol) at rt for 30 min. The reaction mixture was passed through a short column of alumina (petroleum ether) and the solvents were evaporated *in vacuo*. The residue was chromatographed on silica gel (petroleum ether-ether 90:10) to give **24** as an oil (156 mg, 77 %).

^{1}H NMR (500 MHz, $CDCl_3$): 3.89 (1 H, s, HC≡), 4.00 (3 H, s, CH_3), 7.61 (1 H, dt, J= 6.8, 6.8, 1.2 Hz, 6-H), 7.65 (1 H, dt, J=6.8, 6.8, 1.7 Hz, 7-H), 7.87 (1 H, d, J=8.8 Hz, 3-H), 7.87 (1 H, dd, J=7.2, 1.5 Hz, 5-H), 7.95 (1 H, d, J=8.8 Hz, 4-H), 8.59 (1 H, m, ΣJ=14.0 Hz, 8-H).

^{13}C NMR (125 MHz, $CDCl_3$): 52.28 (q, CH_3), 79.57 (s, ≡C-Nph), 88.59 (d, HC≡), 121.26 (s, C-1), 125.52 (d, C-3), 127.15 (d, C-7), 127.57 (d, C-4), 127.72 (d, C-5), 128.28 (d, C-8), 128.78 (d, C-6), 131.57 (s, C-8a), 133.86 (s, C-2), 134.42 (s, C-4a), 167.08 (s, C=O).

IR (CCl_4): 3310 m, 3063 w, 1720 s, 1621 vw, 1594 w, 1567 w, 1506 w, 1278 s, 1260 m, 1245 vs, 1235 s, 975 w, 870 w, 832 w cm^{-1}.

EI MS (m/z, rel. intensity): 210 ($M^{+\cdot}$, 100), 195 (13), 179 (52), 151 (64), 139 (16), 111 (15), 97 (28), 81 (33), 69 (57), 57 (63), 43 (36).

HR EI MS: calcd for $C_{14}H_{10}O_2$ 210.0681, found 210.0683.

Methyl 2-(1-Ethynyl)benzoate 25[20]

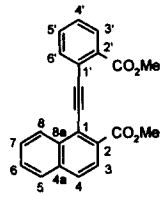
A glass pressure tube with gas inlet was charged with **21** (620 mg, 2.37 mmol) and $Pd(PPh_3)_4$ (137 mg, 0.12 mmol, 5 mol%). The tube was stopped with a rubber septum and flushed with argon. Piperidine (6 mL) was added and the mixture was shortly heated under stirring at 40-50 °C to get a clear solution. After cooling to rt, (trimethylsilyl)acetylene (740 μL, 5.24 mmol, 2.2 equiv) was added. The septum was replaced in a stream of argon with a needle valve which was tightly closed. The reaction mixture was stirred at 80 °C for 2.5 h. The precipitate was filtered off and washed with petroleum petroleum ether (2 x 2 mL). The combined fractions were evaporated to dryness *in vacuo* (at <50 °C) and the residue was chromatographed on silica gel (petroleum ether-ether 95:5) to obtain methyl 2-(2-trimethylsilyl-1-ethynyl)benzoate[21] as an oil (269 mg, 49 %).

Methyl 2-(2-trimethylsilyl-1-ethynyl)benzoate[21] (269 mg, 1.16 mmol) in dry methanol (1 mL) was treated under argon with sodium methoxide (1.39 mmol, 1.2 equiv; 32 mg of sodium dissolved in 1 mL of dry methanol) at rt for 30 min. The reaction mixture was passed through a short column of alumina (petroleum ether) and the solvents were evaporated *in vacuo*. The residue was chromatographed on silica gel (petroleum ether-ether 85:15) to give **25** as an oil (121 mg, 65 %).

^1H NMR (200 MHz, $CDCl_3$) and IR (CCl_4) in accord with the literature data.[20]

EI MS (m/z, rel. intensity): 160 ($M^{+\cdot}$, 91), 129 (100), 101 (79), 75 (42), 57 (20), 51 (22), 43 (25).

Methyl 1-[2-(2-Methyloxycarbonylphenyl)-1-ethynyl]-2-naphthoate 26



Method F: **18** (2.85 g, 10.75 mmol), **25** (1.72 g, 10.74 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (621 mg, 0.54 mmol, 5 mol%), diisopropylamine (30 mL), 80 °C, 50 h. Flash chromatography on silica gel (petroleum ether-ether 85:15 to 80:20) afforded **26** (3.44 g, 93 %).

Mp: 83-84 °C (petroleum ether-acetone).

^1H NMR (500 MHz, $CDCl_3$): 3.99 (3 H, s, CH_3O_2C-Nph), 4.02 (3 H, s, CH_3O_2C-Ph), 7.44 (1 H, dt, J=7.6, 7.6, 1.2 Hz, 4'-H), 7.57 (1 H, dt, J=7.6, 7.6, 1.3 Hz, 5'-H), 7.62 (1 H, ddd, J=8.1, 6.8, 1.2 Hz, 6-H),

7.68 (1 H, ddd, J=8.3, 6.8, 1.4 Hz, 7-H), 7.86 (1 H, d, J=8.5 Hz, 3-H), 7.88 (1 H, dd, J=7.8, 1.5 Hz, 5-H), 7.88 (1 H, dd, J=8.0, 1.2 Hz, 6'-H), 8.00 (1 H, d, J=8.5 Hz, 4-H), 8.05 (1 H, dd, J=7.9, 1.3 Hz, 3'-H), 8.91 (1 H, dq, J=8.5, 1.2, 1.2, 1.2 Hz, 8-H).

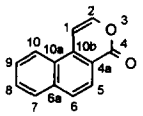
^{13}C NMR (125 MHz, $CDCl_3$): 52.30 (q, $\underline{C}H_3O_2C$-Ph), 52.33 (q, $\underline{C}H_3O_2C$-Nph), 91.16 (s, ≡C-Nph), 99.33 (s, ≡C-Ph), 122.63 (s, C-1), 123.95 (s, C-2'), 127.58 (d, C-3), 128.00 (d, C-5), 128.22 (d, C-4'), 128.26 (d, C-7), 128.33 (d, C-8), 128.42 (d, C-4, C-6), 130.62 (d, C-3'), 130.64 (s, C-1'), 131.62 (s, C-8a), 131.88 (d, C-5'), 133.83 (s, C-2), 134.55 (s, C-4a), 134.72 (d, C-6'),166.73 (s, $CH_3O_2\underline{C}$-Ph), 167.20 (s, $CH_3O_2\underline{C}$-Nph).

IR (CCl_4): 3062 m, 3039 w, 3023 w, 2997 w, 2204 vw, 1731 vs, 1718 vs (sh), 1621 w, 1594 m, 1568 m, 1507 w, 1488 s, 1447 s, 1434 s, 1252 vs, 1243 vs, 969 m cm^{-1}.

EI MS (m/z, rel. intensity): 344 ($M^{+\cdot}$, 30), 329 (87), 298 (20), 279 (100), 270 (30), 248 (27), 220 (18), 150 (20), 119 (20), 91 (17).

HR EI MS: calcd for $C_{22}H_{16}O_4$ 344.1048, found 344.1033.

4*H*-Benzo[*f*]isochromen-4-one 27[22]



Mp in accord with the literature data[22].

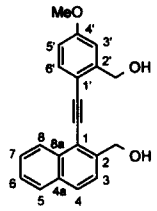
^{1}H NMR (500 MHz, $CDCl_3$): 7.28 (1 H, d, J=5.9 Hz, 1-H), 7.55 (1 H, d, J=5.9 Hz, 2-H), 7.70 (1 H, ddd, J=8.3, 6.1, 1.5 Hz, 9-H), 7.74 (1 H, ddd, J= 8.3, 6.7, 1.2 Hz, 8-H), 7.93 (1 H, bd, J=8.5 Hz, 6-H), 7.96 (1 H, dd, J=7.8, 1.5 Hz, 7-H), 8.25 (1 H, bd, J=8.6 Hz, 5-H), 8.32 (1 H, bd, J=8.3 Hz, 10-H).

^{13}C NMR (125 MHz, $CDCl_3$): 102.73 (d, C-1), 119.18 (s, C-4a), 124.11 (d, C-10), 124.26 (d, C-5), 127.45 (d, C-9), 127.60 (s, C-10a), 128.80 (d, C-6), 128.96 (d, C-7), 129.45 (d, C-8), 135.81 (s, C-6a), 135.92 (s, C-10b), 146.07 (d, C-2), 162.61 (s, C-4).

IR ($CHCl_3$): 3066 w, 1718 vs, 1685 m (sh), 1635 s, 1595 m, 1565 m, 1515 w, 1504 w, 1280 w, 1261 s, 1232 w, 1164 w, 1147 w, 1097 m, 1057 m, 1034 m, 1019 m, 953 w, 930 w, 868 w, 833 m, 805 m, 595 w, 579 w, 543 w, 524 w cm^{-1}.

EI MS (m/z, rel. intensity): 196 ($M^{+\cdot}$, 83), 168 (100), 140 (63), 139 (78), 113 (7), 84 (10), 70 (12), 63 (14), 43 (26).

1-[2-(2-Hydroxymethyl-4-methoxyphenyl)-1-ethynyl]-2-naphthylmethanol 28



Method E: **22** (61 mg, 0.23 mmol), **23** (42 mg, 0.23 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (27 mg, 0.023 mmol, 10 mol%), CuI (5 mg, 0.026 mmol, 10 mol%), diisopropylamine (6 mL), 80 °C, 1 h. Flash chromatography on silica gel (petroleum ether-acetone 70:30) afforded **28** as an amorphous solid (45 mg, 61 %).

^{1}H NMR (500 MHz, $CDCl_3$): 3.87 (3 H, s, CH_3), 4.95 (2 H, s, CH_2-Ph), 5.07 (2 H, s, CH_2-Nph), 6.88 (1 H, dd, J=8.4, 2.6 Hz, 5'-H), 7.05 (1 H, d, J=2.6 Hz, 3'-H), 7.53 (1 H, ddd, J=8.2, 6.9, 1.2 Hz, 6-H), 7.58 (1 H, d, J=8.6 Hz, 3-H), 7.60 (1 H, ddd, J=8.3, 6.9, 1.4 Hz, 7-H), 7.63 (1 H, d, J=8.4 Hz, 6'-H), 7.84 (1 H, bd, J=8.6 Hz, 4-H), 7.86 (1 H, ddt, J=8.2, 1.5, 0.6, 0.6 Hz, 5-H), 8.45 (1 H, ddt, J=8.3, 1.3, 0.8, 0.8 Hz, 8-H).

^{13}C NMR (125 MHz, $CDCl_3$): 55.45 (q, CH_3), 64.47 (t, CH_2-Ph), 64.85 (t, CH_2-Nph), 88.34 (s, ≡C-Ph), 97.37 (s, ≡C-Nph), 113.46 (d, C-3'), 113.49 (d, C-5'), 113.84 (s, C-1'), 119.44 (s, C-1), 125.86 (d, C-3), 126.13 (d, C-8), 126.40 (d, C-6), 127.05 (d, C-7), 128.22 (d, C-5), 128.60 (d, C-4), 132.73 (s, C-4a), 133.30 (s, C-8a), 133.98 (d, C-6'), 140.83 (s, C-2), 144.21 (s, C-2'), 160.21 (s, C-4').

IR ($CHCl_3$): 3609 m, 3475 w, 3060 w, 2840 w, 2198 w, 1605 s, 1566 m, 1508 m (sh), 1497 vs, 1465 m, 1444 w, 1438 w, 1431 m, 1389 w, 1382 w, 1303 s, 1279 m, 1260 m, 1236 s, 1189 w, 1162 m, 1114 w, 1059 m, 1040 m, 1025 m, 1014 m, 879 w, 861 w, 822 s, 694 w, 543 m cm^{-1}.

EI MS (m/z, rel. intensity): 318 ($M^{+\cdot}$, 6), 300 (9), 285 (6), 277 (100), 262 (10), 201 (15), 199 (17), 183 (20), 152 (11), 97 (7), 77 (16), 71 (9), 69 (9), 57 (14), 55 (9), 51 (10), 43 (10).

HR EI MS: calcd for $C_{21}H_{18}O_3$ 318.1256, found 318.1263.

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15. Alternatively, an insertion into the aryl C-H bond in **B** (Scheme 2) to form a palladium(IV) intermediate followed by proton abstraction by base to get the palladacycle **D** may take place.[14]

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